

ICONN 2015 [4th - 6th Feb 2015]

International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

A First Principles Study on the Adsorption of CO Molecule on Rh₄ and Rh₃X clusters

P.Munieswaran¹, S. Seenithurai¹, R. Kodi Pandyan¹,
S. Vinodh Kumar¹, M. Mahendran^{1*}

¹Smart Materials Lab, Department of Physics, Thiagarajar college of Engineering,
Madurai – 625005, India.

Abstract: We have investigated the electronic structure of Rh₄ and Rh₃X (X= Sc and V) cluster and performed a comparative study on the adsorption of CO molecule on them by using density functional theory (DFT). The adsorption has been analyzed on two different sites of Rh₄ and Rh₃X clusters. The adsorption binding energy of CO on Rh₃V and Rh₃Sc clusters is found to be greater than on the Rh₄ cluster. The Rh top of the Rh₃-Sc cluster strongly binds CO molecule with a binding energy of 2.49 eV. The polarization of clusters has been analyzed before and after the adsorption of gas molecules by using Hirshfeld charge analysis. The HOMO and LUMO gaps have been calculated. The results show that Rh and Rh-based alloys are very useful in gas sensors applications and catalytic activities.

Keywords: Adsorption, CO Molecule, Rh₄, Rh₃X clusters.

Introduction

Rhodium plays an important role as three way catalyst¹. Adsorption of CO molecule on small Rh_x clusters was studied by depositing on thin alumina film by infrared reflection spectroscopy^{2,3,4,5}. Theoretically, the adsorption of CO molecule on Rh cluster has been studied with different approaches and geometry optimized structure, electronic structure and vibrational frequencies of RhCO and Rh(CO)₂ have also been reported^{6,7,8,9,10}. The modification of the adsorption binding energies, preference of the site and the stability of CO+H₂ were reported by using DFT calculation¹¹. Rh is found to be effectively improve the selectivity/adsorption and fabrication of C₂ oxygen-containing compounds (such as CH₃COOH, C₂H₅OH and CH₃CHO)¹². The aim of this paper is to understand the adsorption of CO molecule on tetrahedral (Rh₄, Rh₃V and Rh₃Sc) structure. Further, we have computed an electronic structure, average binding energy, HOMO – LUMO energy gap of CO adsorbed tetrahedral clusters and on Sc/V doped Rh clusters.

Computational details

The geometry optimization and energy calculations were performed by the Density Functional Theory using the Dmol³ package. The Generalized Gradient Approximation with Perdew – Wang exchange correlation functional was used. Effective core potential with double numerical polarization basis sets was used for core treatment and maximum force and displacements were set to 0.002 Ha/Å and 0.004 Å respectively. For accurate result, we use a SCF tolerance of 10⁻⁶ Ha and octupole multipolar expansion scheme was used in our

calculation. The average binding energy of the optimized Rh₄, Rh₃V and Rh₃Sc clusters were calculated by using the expression

$$E_b = (nE_{\text{Atom}} - E_{\text{Cluster}}) / n \quad (1)$$

Where, n is the number of metal atoms, E_{atom} is the total energy of the Rh/V/Sc atoms and E_{cluster} total energy of the metal cluster. The adsorption energy of the Rh₄/Rh₃V/Rh₃Sc– CO clusters are calculated using the equation

$$E_{\text{ad}} = (E_{\text{cluster}} + E_X - E_{\text{cluster}+X}) \quad (2)$$

E_{cluster+X} are the total energy of the metal cluster with gas adsorption and E_X is energy of gas molecule.

Results and Discussion

Rh₄ and Rh₃V and Rh₃Sc Cluster Structures

By using DFT, the structure of Rh₄ and Rh₃X (Sc and V)clusters were optimized. There are a number of papers which reported on average binding energy, adsorption energy and HOMO–LUMO energy gap on Rh₄ cluster. In our present work, the average binding energy and HOMO – LUMO gap for tetrahedral structure were calculated by using DMol3 code and found to be 2.39 eV and 1.16 eV respectively. The geometry optimized structure and corresponding bond length distance are shown in the Figure 1(i). The Rh –Rh bond length distance is 2.49 Å in Rh₄ tetrahedral structure. The geometrical isomer of Rh₃V and Rh₃Sc was observed by replacing one Rh atom of the Rh₄ cluster with a V and Sc atoms as shown in Figure 1 (ii) and (iii). The average binding energy increases from 2.39 eV to a value of 2.48 eV when V is doped. A large change is observed from 2.39 to 2.97 when Sc is doped. The HOMO – LUMO energy gap for Rh₃V is 0.50eV and it is 0.79eV for Rh₃Sc. The three Rh – Rh bond lengths are 2.69 Å, 2.68 Å and 2.66 Å for Rh₃V and 2.58 Å, 2.53 Å and 2.59 Å for Rh₃Sc cluster. The corresponding average binding energy and HOMO – LUMO energy gaps are provided in Table 1.

Table I. Calculated average binding energy (eV) and HOMO – LUMO energy gaps (eV) of Rh₄, Rh₃V and Rh₃Sc tetrahedral clusters.

Structure	Average binding energy (eV)	HOMO – LUMO energy gap (eV)
Rh ₄ – Tetrahedral	2.39	1.16
Rh ₃ V – Tetrahedral	2.48	0.50
Rh ₃ Sc – Tetrahedral	2.97	0.79

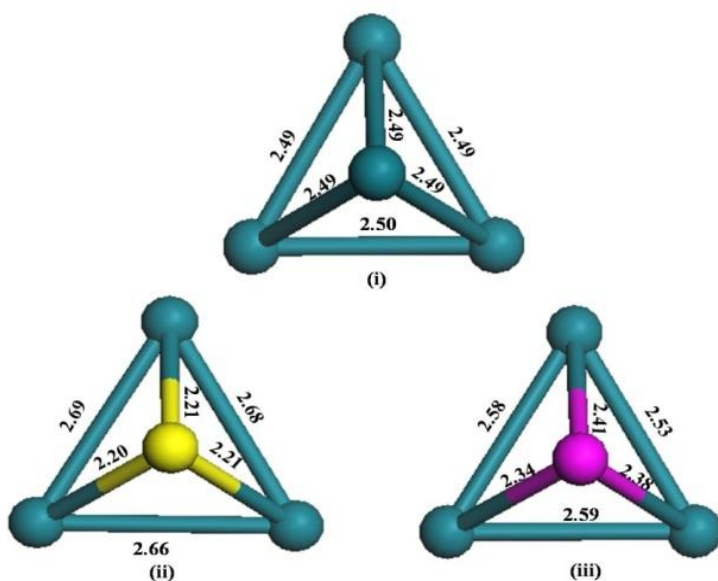


Figure 1. Optimized structure of tetrahedral (i) Rh₄, (ii) Rh₃V and (iii) Rh₃Sc clusters. Rh, V and Sc is shown in blue, yellow and Pink.

Adsorption of CO molecule on Rh₄ Cluster

For the adsorption of CO molecule on Rh₄ cluster, three possible approaches - (i) CO – bonded on Rh top (ii) CO – bonded on Rh – Rh bridge and (iii) CO – bonded on Rh – Rh – Rh centre on both Head and side on orientation structure - were considered. The corresponding geometry optimized structures, the bond length of CO, the adsorption energy and HOMO – LUMO energy gap of Rh₄ - CO cluster are given table II and III. The adsorption of CO molecule on Rh₄ cluster (Rh – Rh bridge site in Head on approach) has more adsorption energy (2.23eV) than in Rh₄ cluster. The corresponding geometry structures along with the bond length are shown in Figure 2

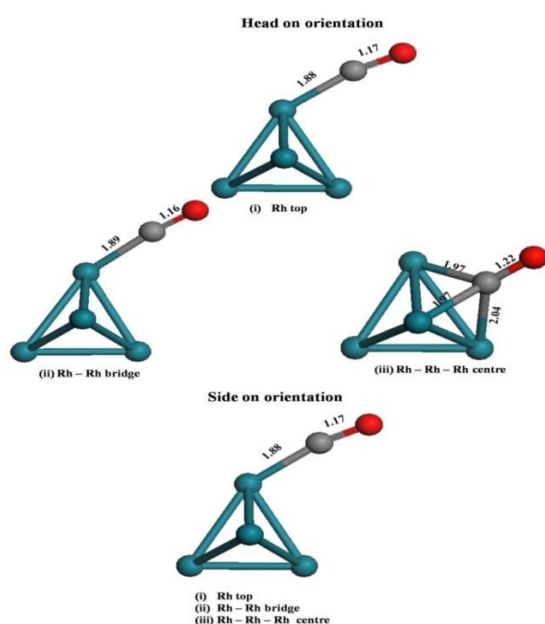


Figure 2. The optimized structures of CO adsorption on Rh₄ cluster at head and side on approach.

Adsorption of CO molecule on Rh₃V and Rh₃Sc Clusters

The adsorption of CO molecule on both head and side on orientation of Rh₃V and Rh₃Sc clusters is possible in five different configuration (i) CO – bonded on Rh top (ii) CO – bonded on V/Sc top (iii) CO – bonded on Rh – Rh bridge (iv) CO – bonded on Rh – V/Sc bridge (v) CO – bonded on Rh – V/Sc – Rh centre. The corresponding optimized structures, the bond length of CO elongation, the adsorption binding energy and HOMO – LUMO energy gap corresponding to Rh₃V– CO and Rh₃Sc– CO clusters are listed out in table II and III respectively. The adsorption of CO molecule (Rh top approach) on Rh₃Sc cluster has more adsorption binding energy (2.49eV) compare to all other optimized structures. The corresponding geometry optimized structures along with the bond length are shown in Figure 3 (a) head and (b) side on orientation for Rh₃V - CO and 4 (a) head and (b) side on orientation for Rh₃Sc - CO. The spin resolved partial density of states of Rh₃Sc and Rh₃Sc - CO clusters, show that adsorption is due to the charge transfer from CO molecule to metal surface cluster (i.e. σ electron density) and τ back donation of electron which is known as the Blyholder mechanism. Changes in the partial density of states (PDOS) in d - orbitals are observed for both structures. States are induced from -2 to -6eV below the Fermi level for Rh₃Sc – CO system. The corresponding partial density of states (PDOS) vs energy level graph are shown in Fig 5(a and b).

Table II. Calculated adsorption energy (eV) of CO molecule on Rh₄, Rh₃V and Rh₃Sc cluster systems (head on orientation)

Structure	Initial approach	Adsorption energy (eV)	d _{C-O}	HOMO – LUMO energy gap (eV)
Rh ₄ – CO	Rh - top	2.17	1.17	0.77
Rh ₄ – CO	Rh – Rh bridge	2.23	1.16	0.74
Rh ₄ – CO	Rh – Rh – Rh face	2.11	1.22	0.04
Rh ₃ V – CO	Rh - top	2.42	1.17	0.93

Rh ₃ V –CO	V - top	1.28	1.16	0.24
Rh ₃ V –CO	Rh – Rh bridge	2.14	1.20	0.18
Rh ₃ V –CO	Rh – V bridge	1.88	1.20	0.61
Rh ₃ V –CO	Rh – V – Rh face	1.86	1.22	0.63
Rh ₃ Sc –CO	Rh - top	2.49	1.17	0.89
Rh ₃ Sc –CO	Sc - top	0.58	1.15	0.58
Rh ₃ Sc –CO	Rh – Rh bridge	2.44	1.21	1.11
Rh ₃ Sc –CO	Rh – Sc bridge	1.75	1.20	0.86
Rh ₃ Sc –CO	Rh – Sc – Rh face	2.36	1.21	0.83

Table III. Adsorption energy (eV) and bond length (d_{C-O}) of CO molecule on Rh₄, Rh₃V and Rh₃Sc cluster systems (side on orientation).

Structure	Initial approach	Adsorption energy (eV)	d _{C-O}	HOMO – LUMO energy gap (eV)
Rh ₄ – CO	Rh - top	2.17	1.17	0.80
Rh ₄ – CO	Rh – Rh bridge	2.18	1.17	0.75
Rh ₄ – CO	Rh – Rh – Rh face	2.17	1.17	0.75
Rh ₃ V –CO	Rh - top	2.37	1.17	0.55
Rh ₃ V –CO	V - top	0.64	1.20	0.60
Rh ₃ V –CO	Rh – Rh bridge	2.35	1.17	0.56
Rh ₃ V –CO	Rh – V bridge	2.38	1.17	0.54
Rh ₃ V –CO	Rh – V – Rh face	2.15	1.19	0.26
Rh ₃ Sc –CO	Rh - top	2.43	1.17	0.87
Rh ₃ Sc –CO	Sc - top	0.17	1.16	0.43
Rh ₃ Sc –CO	Rh – Rh bridge	2.42	1.21	0.99
Rh ₃ Sc –CO	Rh – Sc bridge	2.46	1.17	0.77
Rh ₃ Sc –CO	Rh – Sc – Rh face	2.40	1.21	1.17

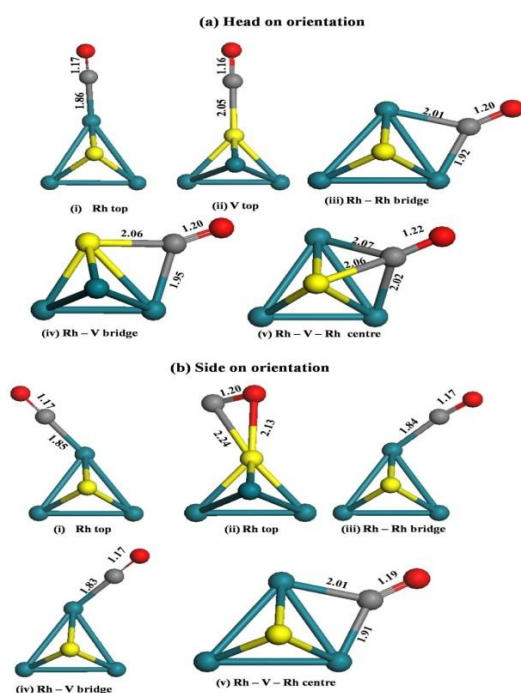


Figure 3. Optimized structures of CO adsorbed Rh₃V clusters at both head and side on orientation. C and O are shown in grey and red colored balls.

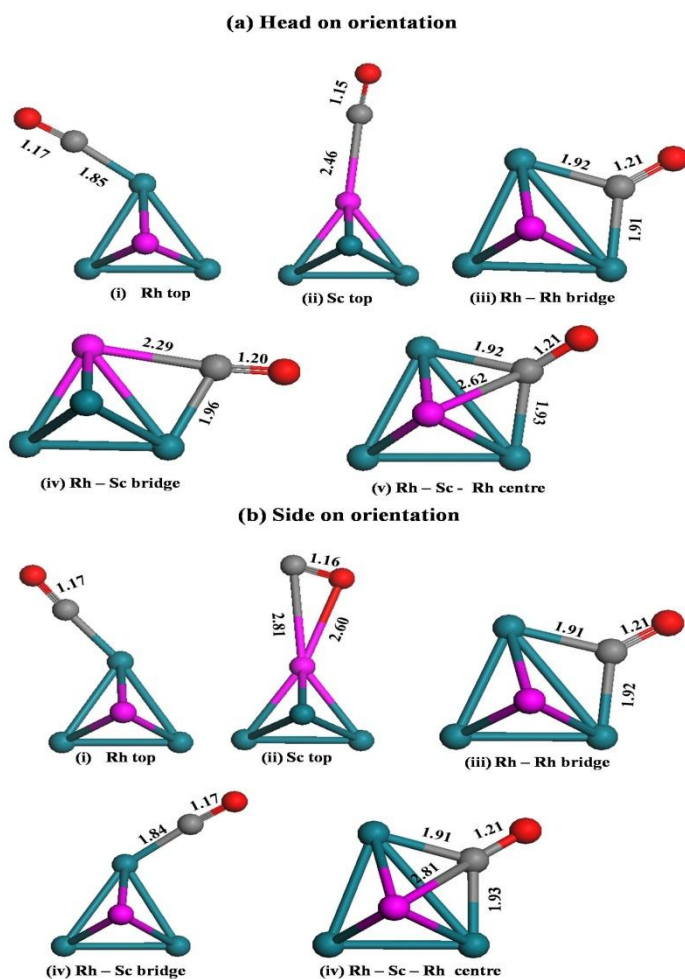


Figure 4. Optimized structures of CO adsorbed Rh₃V clusters at both (a) head and (b) side on orientation.

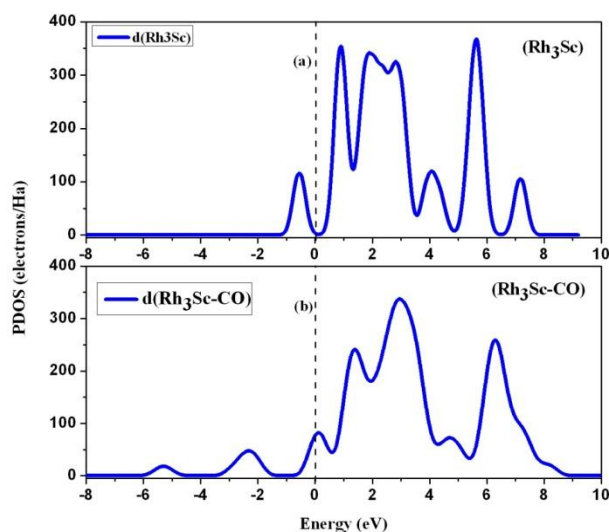


Figure 5. Partial density of states of (a) d – orbitals on Rh₃Sc without CO molecule (b) d – orbitals in Rh₃Sc – CO system.

Hirshfeld Charge:

The Hirshfeld charge has been used to find the charge transfer from gas molecule to metal surface. The charges were analyzed in the optimized structures of Rh₄, Rh₃V and Rh₃Sc clusters before and after the

adsorptions and the values are listed out in the Table IV. Initially, the charge of each Rh atom has zero in Rh₄ cluster. After the CO adsorption, transfer of charge occurs from Rh atom to C atom leading to the total positive charge on Rh atom in Rh₄ – CO structure. In Rh₃V/Sc cluster, due to the electronic charge flow from V/Sc to Rh, all the Rh atoms are negatively charged and the single V/Sc atom is positively charged. For CO adsorption, the C atom is directly attached to the Rh top site in Rh₃Sc – CO has more positive charge than Rh₃V – CO cluster as seen in the table IV. In both molecular adsorptions, the Sc atom has more positive charge compared to its original value. Therefore, after adsorption of gas molecule the cluster becomes polarized. The symbol ‘*’ in the table indicates that the CO molecule binds with that particular atom.

Table III. Hirshfeld charges before and after the adsorption of CO molecule on clusters for high adsorption binding energy cases only.

Hirshfeld charge			
CO			
C1 0.0715		O2 - 0.0714	
Rh ₄		Rh ₄ - CO	
Rh1	0	Rh1	-0.0573
Rh2	0	Rh2	0.0550
Rh3	0	Rh3	0.0724
Rh4	0	*Rh4	0.0501
		*C1	0.0182
		O2	-0.1386
Rh ₃ V		Rh ₃ V - CO	
Rh1	-0.0259	Rh1	0.0016
Rh2	-0.0239	Rh2	-0.0099
Rh3	-0.0244	*Rh3	-0.0036
V4	0.0742	V4	0.1668
		*C1	-0.0028
		O2	-0.1524
Rh ₃ Sc		Rh ₃ Sc - CO	
Rh1	-0.0759	Rh1	-0.0213
Rh2	-0.0847	Rh2	0.0002
Rh3	-0.0822	*Rh3	-0.1247
Sc4	0.2428	Sc4	0.3161
		*C1	-0.0081
		O2	-0.1619

Conclusion

The geometry optimized structure, adsorption binding energy (E_b), and HOMO – LUMO energy gap (E_g) of CO molecules adsorbed Rh₄, Rh₃V and Rh₃Sc cluster have been studied by using density functional theory (DFT). The adsorption binding energy of CO molecule on (Rh top) Rh₃Sc cluster was higher than in other clusters. The charge transfer is large in Rh₃Sc (2.49 eV for CO molecule on Rh top) compared to Rh₄ and Rh₃V clusters. The electronic charge transfer between the molecule and the metal cluster has been discussed by Hirshfeld charge. It is found that the cluster becomes more polarized after CO adsorption. We conclude that the Rh and Rh-based alloys could be useful for catalytic activity and gas sensor applications.

Acknowledgement

One of the authors (MM) would like to thank the DST, New Delhi, for the financial support of DMol³ code, through Fast Track Young Scientist Award.

References

1. Satterfield, C.N., Heterogeneous Catalysis in Industrial Practice, 2nd ed. Krieger, Malabar, 1996.
2. Jaeger, R.M., Kuhlbeck, H., Freund, H.J., Wuttig, M., Hoffmann, W., Francy, R., Ibach, H., Structure and defects of an ordered alumina film on NiAl(110), Surf. Sci., 1994, 61. 318.

3. Freund, H.J., Adsorption of Gases on Complex Solid Surfaces, *Angew. Chem., Int. Ed. Engl.*, 1997, 36, 452.
4. Frank, M., Kuhnemuth, R., Baumer, M. and Freund, H.J., Vibrational spectroscopy of CO adsorbed on supported ultra-small transition metal particles and single metal atoms, *Surf. Sci.*, 2000, 468, 454-456.
5. Frank, M., Baumer, M., Kuhnemuth, R., Freund, H.J., Metal atoms and particles on oxide supports: probing structure and charge by infrared spectroscopy, *J. Phys. Chem. B.*, 2001, 105, 8569.
6. Barnes, L.A., Rosi, M., Bauschlicher, C.W. Jr., Theoretical studies of the first- and second-row transition-metal mono- and dicarbonyl positive ions, *J. Chem. Phys.*, 1990, 93, 609.
7. Papai, I., Goursot, A., St-Amanat, A., Salahub, D.R., Density Functional Study of Mono- and Di-Carbonyls of Palladium and Rhodium, *Theor. Chim. Acta.*, 1992, 84, 217.
8. Dai, D. and Balasubramanian, K., Potential-Energy Surfaces for Rh-CO, Rh-OC, Ir-Co, and Ir-OC Interactions, *J. Chem. Phys.*, 1994, 101, 2184.
9. McKee, M.L. and Worley, S.D., Ab initio study of the interaction of rhodium with dinitrogen and carbon monoxide, *J. Phys. Chem. A.*, 1997, 101, 5600.
10. Zhou, M. and Andrews, L., Reactions of Laser-Ablated Co, Rh, and Ir with CO: Infrared Spectra and Density Functional Calculations of the Metal Carbonyl Molecules, Cations and Anions in Solid Neon, *J. Phys. Chem. A.*, 1999, 103, 7773.
11. Ma, X., Deng, H., Yang, M.M., and Li, W., Atomic and molecular adsorption on RhMn alloy surface: A first principles study, *J. Chem. Phys.*, 2008, 129, 244711.
12. Bhasin, M.M., Bartley, W.J., Ellgen, P.C., and Wilson, T.P., Synthesis gas conversion over supported rhodium and rhodium-iron catalysts, *J. Catal.*, 1978, 54, 120.
